SESQUITERPENE LACTONES OF Pyrethrum pyrethroides.

III. ISOPYRETHROIDININ

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Continuing a study of the total chloroform extract of the epigeal part of Pyrethrum pyrethroides (Kar. et Kir.) B. Fedtsch. ex Krasch. [1, 2] collected in the period of full flowering in the Tadzhk SSR, we have isolated a new sesquiterpene lactone with the composition $C_{15}H_{20}O_4$, mp 143-145°C (ethyl acetate–hexane), $[\alpha]_D^{22}$ −69,5° (c 0,27 ; ethanol), which we have called isopyrethroidinin (I).

The IR spectrum of (I) (KBR) had absorption bands at 3330 cm^{-1} (OH) and 1775, 1660, and 1630 cm^{-1} (C=O of an α,β-unsaturated γ-lactone; conjugated and isolated C=C bonds). The UV spectrum was characterized by a maximum at $\lambda^{C_2H_5OH}$ 204 nm (log ε 4.25). The circular dichroism spectrum (C_2H_5OH) showed a negative Cotton effect at 254 nm (Δε = −0.83).

The following ion peaks were observed in the mass spectrum of (I), m/z (%): M^+ 264 (2, 4) 249 (6.3), 246 [M^+ −H_2O] (19), 231 (16.5), 228 [M^+ −$2H_2O$] (26), 218 (24.7), 213 (20), 204 (14), 203 (19), 201 (15.8), 199 (16.5), 191 (19.1), 190 (14.6), 189 (17), 188 (17), 187 (10.7), 186 (14), 185 (28.5), 91 (100), indicating that isopyrethroidinin belonged to the guaianolide series and that its molecule contained two hydroxy groups.

In the PMR spectrum of (I) taken in C_5D_5N, the signals of the protons of the hydroxy groups appeared at 6.44 ppm in the form of a doublet with ^3J = 4 Hz and a singlet at 5.87 ppm. Consequently, one of them was secondary and the other tertiary.

The PMR spectrum of (I) taken in $CDCl_3$ (0 – HMDS, H_2 – 200 MHz) contained the signals of the protons of one methyl group in a CH_3–C–OH fragment – a 3H singlet at 1.13 ppm – and of two exocyclic methylene groups: at a lactone ring – doublets of 1 H each at 5.42 and 6.16 ppm with ^4J = 2.4 and 3.5 Hz, respectively – and in the main guaiane skeleton – triplets of 1 H each at 5.31 and 5.39 ppm with $\Sigma J \cong 3$ Hz. The lactone proton resonated at 3.95 ppm and was characterized by a triplet with Σ^3J = 21 Hz, which was due to its trans-diaxial spin-spin coupling with the vicinal H-5 and H-7 atoms.

Double proton-proton experiments showed that there was no spin-spin coupling between the proton at the secondary hydroxy group and the lactone proton, and a triplet with broadened lines at 3.06 ppm corresponded to H-5 and a quartet signal at 2.52 ppm with Σ^3J = 24 Hz and with a ratio of the relative intensities of the lines of 1:3:3:1 corresponded to H-1.

These facts, and also the chemical shifts of the protons of the exocyclic methylene group at the lactone ring of 5.42 and 6.16 ppm indicating the absence of a hydroxy substituent at C-8 [5] showed the trans linkage of the lactone ring at C-6 and C-7 of the guaiane skeleton and the position of the secondary hydroxy group at C-3 of isopyrethroidinin molecule.

It is known from literature sources that in such guaiane systems containing a secondary hydroxy group at C-3 the protons of the exocyclic methylene group at C-4 resonate in a weaker field (5.3-5.5 ppm) than those at C-10 (4.7-5.1 ppm) [6-12]. In the PMR spectrum of the lactone under investigation the protons concerned are characterized by signals at 5.31 and 5.39 ppm. It may be concluded from this that the exocyclic methylene group in the main skeleton of the isopyrethroidinin molecule is located at C-4 and the CH_3–C–OH fragment is formed at C-11.

Thus, the experimental results given above have permitted the suggestion that the iso-

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*Deceased.

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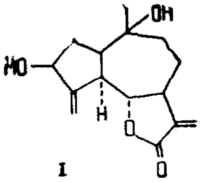
pyrethroidinin structure corresponds to 3,10-dihydroxy-1,5α,7α(H)6β(H)-guaia-4(15),11(13)-dien-6,12-olide.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LITERATURE CITED

1. B. Kh. Abduazimov, A. I. Yunusov, and G. P. Sidyakin, Khim. Prir. Soedin., 649 (1983).
2. B. Kh. Abduzimov, N. D. Abdullaev, A. I. Yunisov, M. R. Yagudaev, and G. P. Sidyakin, Khim. Prir. Soedin., 792, (1984).
3. U. A. Abdullaev, Ya. V. Rashkes, M. I. Yusupov, and Sh. Z. Kasymov, Khim. Prir. Soedin., 796 (1980).
4. U. A. Abdullaev, Ya. V. Rashkes, I. D. Sham'yanov, and G. P. Sidyakin, Khim. Prir. Soedin., 56 (1982).
5. H. Voshioka, T. J. Mabry, M. A. Irwin, T. A. Geissman, and Z. Samek, Tetrahedron, 27, 3317 (1971).
6. F. Bohlmann and C. Zdero, Phytochemistry, 16, 778 (1977).
7. A. G. Gonzales, J. Bermejo, I. Cabrera, G. M. Massanet, H. Mansilla, and A. Galindo, Pytochemistry, 17, 955 (1978).
8. P. S. Kalsi, V. B. Sood, A. B. Masih, D. Gupta, and K. K. Talwar, Phytochemistry, 22, 1387 (1983).
9. S. Das, R. N. Baruan, R. P. Sharma, I. N. Baruan, and P. Kulanthivel, W. Herz, Phytochemistry 22, 1980 (1983).
10. P. S. Kalsi, Sunila Sharma, and Gurdeep Kaur, Phytochemistry, 22, 1993 (1983).
11. S. Oksur and E. Putun, Phytochemistry, 22, 2615 (1983).
12. K. Ito, T. Iido, and T. Kobayashi, Phytochemistry, 23, 188 (1984).

α-BISABOLOL IN NEEDLES OF THE FAMILY Pinacae

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The sesquiterpence alcohol α-bisabolol has been found in the needles of a number of conifers of the family Pinaceae [1] . However, no attention was devoted to which of the four stereoisomers was present in a particular oleoresin. In some cases — for example, for the biogenesis of bisabolol, for the chemotaxonomy of conifers, and for synthetic organic chemistry — the stereoisomeric forms of α-bisabolol may play an important role. The determination of the configurations of the asymmetric carbon atoms of α-bisabolol is a fairly complex problem, but it has been solved by a number of workers using synthesis from known compounds [2]. It follows from these investigations that (+)-α-bisabolol has the 6S configuration, and the (—) form the 6R configuration. The configuration at the carbinol carbon atom (C_7) can be determined from the position of the C_7 methyl group in the PMR spectrum — for 6S,7R- and 6R,7S-α-bisabolols the signals of this group are observed in a weaker field than for the other diasteromers of α-bisabolol (the 6S,7S- and 6R,7R-isomers) [2].

On investigating; the α-bisabolols isolated from six species of conifers: Pinus sibirica ($[\alpha]_D^{19}$ +50° (c 4,8; $CHCl_3$)) ; Pinus koraiensis ($[\alpha]_D^{20}$ +49,4° (in the pure form)); Picea ajanensis ($[\alpha]_D^{24}$ +43° (c 3,25; $CHCl_3$)) ; Abies sibirica ($[\alpha]_D^{20}$ +62° (in the pure form)); Abies semenovii ($[\alpha]_D^{22}$ +62° (in the pure form)), and Abies nephrolepis ($[\alpha]_D^{22}$ +70° (c 1,7; $CHCl_3$)),— we found that all the oleoresins mentioned contained dextrorotatory α-bisabolol. Thus, they must have the 6S configuration in all cases. In the PMR spectra of the α-bisabolols isolated

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